

Field, Laboratory and Model Studies of CDOM

Neil V. Blough

Department of Chemistry and Biochemistry

University of Maryland

College Park, MD 20742

phone: (301) 405-0051 fax: (301) 314-9121 email: nb41@umail.umd.edu

Daniel E. Falvey

Department of Chemistry and Biochemistry

University of Maryland

College Park, MD 20742

phone: (301) 405-1808 fax: (301) 314-9121 email: df37@umail.umd.edu

Award Number: N00014-02-1-0654

<http://www.chem.umd.edu/ane/blough/index.html>

http://www.chem.umd.edu/organic/falvey/falvey_home.html

LONG-TERM GOALS

The principal long-term objective of this work is to determine what factors control the distribution and dynamics of the chromophore-containing constituents of dissolved organic matter (CDOM) in marine and estuarine waters. Two important secondary objectives are 1) to elucidate the photochemical properties of the CDOM and how photochemical reactions affect the optical properties and secondary reactivity of the CDOM, 2) to obtain a clearer understanding of the nature of the underlying light-absorbing constituents that produce the absorption spectrum of the CDOM. Field measurements are employed to determine the distribution of CDOM and its impact on the aquatic light field, whereas a combination of field and laboratory experiments are used to test mechanisms of its formation and loss. Model systems are being employed to probe the nature of the constituents giving rise to the observed absorption spectrum of CDOM.

OBJECTIVES

Over the last year, our principal near-term objectives were as follows:

1. Complete the analysis and synthesis of field data collected over the last five years and prepare manuscripts for publication.
2. Acquire and analyze data from a set of laser photobleaching experiments; prepare manuscript on this topic.

APPROACH

Over the past five years, we have carried out a systematic series of field studies examining the distribution of CDOM in the Middle Atlantic Bight (MAB) and the Delaware and Chesapeake Bays over the late Spring and Summer and into early Fall. The objectives of these studies were 1) to

determine the spatial and seasonal contribution of CDOM absorption to the total light absorption in the UV and visible spectral ranges, 2) to infer sources and sinks of CDOM based on changes in its spatial and temporal distributions, and 3) to examine the effects of water-column stratification on the distribution and magnitude of CDOM absorption on the shelf of the MAB over the summertime. The results and conclusions of these studies, which are detailed in Del Vecchio (2002) and a manuscript (Del Vecchio and Blough, in preparation; Del Vecchio et al., in preparation), are summarized below.

Both field and laboratory studies have been used to investigate the sources and sinks of CDOM in the marine environment. For example, field measurements first indicated that photochemistry could act as a significant sink of CDOM in stratified surface waters over the summer (Vodacek et al., 1997), with more recent studies supporting these conclusions (Del Vecchio and Blough, in preparation). Laboratory photobleaching studies have been employed to test whether the time scale of this process and the changes in CDOM spectral shape are compatible with the field observations (Del Vecchio and Blough, 2002).

Because we know almost nothing about the structural nature of the underlying chromophores giving rise to the rather unique absorption spectrum of the CDOM, we have initiated a series of laboratory studies aimed at addressing this issue. Techniques that we are employing include laser photobleaching experiments of CDOM in high viscosity solvents, and the analysis of the absorption spectra of mixtures of small molecules in solution.

WORK COMPLETED

1. The analysis of field data collected over the last six years has been completed, with two manuscripts in preparation for submission to a special edition of Marine Chemistry on CDOM (Del Vecchio and Blough and Del Vecchio et al.).
2. A major review article on the distribution and dynamics of CDOM was published (Blough and Del Vecchio, 2002), as was a detailed study on photobleaching of CDOM (Del Vecchio and Blough, 2002). A second, more general review, developed from an invited NATO talk (Del Vecchio), has been accepted for publication (Del Vecchio and Blough, in press).
3. A complete set of laser photobleaching experiments at wavelengths covering the visible and ultraviolet wavelengths has been collected and analyzed; a manuscript on this topic is also nearly completed.

RESULTS

First, our field work has shown that CDOM always dominates total light absorption in the UV-B and UV-A relative to particulate material (phytoplankton and detritus) for coastal surface waters of the MAB, with the relative contribution of CDOM increasing offshore (to >90%). At longer wavelengths (438 nm), the contribution of CDOM and phytoplankton absorption to the total light absorption was comparable particularly in May and October, with detrital material absorption always representing the least absorbing component except in Bay waters. The lack of a clear correlation between CDOM and phytoplankton absorption at 438 nm suggests that phytoplankton do not represent a significant, immediate source of CDOM in Bay waters; the better correlations observed on the shelf of the MAB in the summer suggests that phytoplankton might act as a very weak source of CDOM, although the evidence supporting this possibility is not very strong.

Second, although a linear relationship between CDOM absorption and fluorescence was observed on the shelf of the MAB consistent with past results (Vodacek et al., 1997), this relationship showed a slight upward curvature for the higher values observed in the Delaware and Chesapeake Bays, suggesting either the presence of slightly different CDOM source(s) with higher fluorescence efficiencies and/or the occurrence of (photo)chemical/biological processing of the CDOM during transit down the Bays.

Third, the absence of substantial curvature in plots of CDOM absorption versus salinity for Bay waters indicates that there are no large *in situ* sources or sinks of CDOM within the Bays, and that the CDOM is largely of terrestrial origin. However, the variation of the absorption to fluorescence ratio (see above), as well as the small deviations from linearity in the mixing curves, indicates that the observed dependence of CDOM absorption on salinity cannot rigorously be attributed to the simple dilution of a single terrestrial end-member. The poor correlation between CDOM and phytoplankton absorption noted above, however, indicates that direct *in situ* input of CDOM from phytoplankton is very small or non-existent. Thus, the CDOM in this region is primarily terrestrial in origin.

Fourth, a strong seasonal sink of CDOM is clearly evident in the surface waters of the MAB shelf. In the July, August and September cruises, CDOM absorption in surface waters decreased rapidly over a very small salinity range, while absorption in the deeper waters below the thermocline was much higher, falling close to the mixing line extrapolated from the Delaware Bay. Further the spectral slope, S , of the surface waters increased relative to the deep waters, and the ratio of CDOM absorption to DOC concentration was much lower than that of the underlying waters. In contrast, this behavior was not observed in May when stratification was not as fully developed and the solar irradiance was lower, nor was it observed in October when stratification was lost due to a prior storm. These data point to a strong photochemical sink of CDOM in the surface waters of the MAB shelf over the summer. The absence of a readily observable photochemical sink in Bay waters is explainable by the higher CDOM absorption within these regions. In these regions, photobleaching is restricted to a very shallow surface layer (due to the high CDOM absorption), and the effects of the photobleaching averaged over a larger mixing depth. Only when the CDOM absorption is diluted to the point where the average penetration depth of the photochemically-active wavelengths becomes comparable to the mixed layer depth does the photobleaching become evident. This condition applies on the shelf over the summertime when the diluted CDOM is constrained in a shallow mixed layer. Overall, these results show that photobleaching can be a substantial, if not the dominant, sink of CDOM in surface waters.

To test whether photobleaching could account for the spectral changes and the magnitude of the absorption loss in surface waters over the summer, a detailed laboratory study of the photobleaching kinetics of a Suwannee River fulvic acid standard and two waters from the Chesapeake and Delaware Bays were undertaken, employing both monochromatic and polychromatic light sources (Del Vecchio and Blough, 2002). The kinetics of CDOM absorption loss at a series of monochromatic irradiation wavelengths were employed to create a simple, heuristic model of photobleaching. This model allowed us to predict the kinetics of photobleaching of CDOM under polychromatic light fields. Application of this model to natural waters predicted well the change in the spectral slope (S) caused by photodegradation. Further, the predicted time scale of the photobleaching was consistent with our field observations of shelf waters in the MAB over the summer. As suggested above, the results of the modeling indicates that the ratio of the photodegradation depth to the mixed layer depth is a key parameter controlling the rate of photobleaching in surface waters. When the average photodegradation depth is very small with respect to the mixed layer depth, only small absorption losses and little change

in S is observed. In contrast, when the average photodegradation depth is comparable to or greater than the mixed layer depth, a more rapid loss of absorption and larger increases in S are observed, consistent with past field studies (Blough and Del Vecchio, 2002). When the ratio of the photodegradation to mixed layer depth increases either through dilution or photobleaching, the loss of CDOM absorption in surface waters accelerates.

An analysis of the monochromatic bleaching kinetics first indicated to us that a model based on a simple superposition of numerous chromophores undergoing photobleaching independently could not apply (Del Vecchio and Blough, 2002). This conclusion further implies that the absorption spectrum of CDOM cannot arise solely from a simple superposition of the spectra of numerous independent chromophores. Instead, these results suggest that there must be electronic coupling between chromophores. To further test this possibility, a series of ‘hole-burning’ experiments were conducted to study the nature of the species that produces the absorption spectrum of humic substances and CDOM (Del Vecchio and Blough, in preparation). A high intensity Nd-YAG laser or a Nd-YAG laser pumping a dye laser was employed to destroy selectively species absorbing at specific wavelengths across the UV and visible wavelengths, with the time course of the absorption losses followed across the entire UV/visible spectrum. To suppress or eliminate the possible effect of reactive oxygen species and secondary photochemistry on the photodegradation, samples were prepared in a high viscosity solvent (90% glycerol/water). The results of these experiments, although too extensive to describe here, show unequivocally that the absorption spectrum of humic substances cannot be explained as a simple sum of the absorption spectra of numerous **independent** chromophores (Del Vecchio, 2002; Del Vecchio and Blough, in preparation).

IMPACT APPLICATIONS

Because CDOM contributes significantly to the absorption of coastal and offshore waters, its presence substantially impacts underwater visibility and the aquatic light field. Thus an understanding of its sources and sinks, as well as the nature of the light-absorbing constituents contributing to its spectrum, are needed to predict its spatial and temporal variability in coastal (and open-ocean) waters.

TRANSITIONS

In collaboration with other ONR-supported PIs, we are preparing manuscripts for submission to a special edition of Marine Chemistry on CDOM.

RELATED PROJECTS

In other ONR-supported work just completed, we examined mechanistic aspects of the photochemistry of CDOM and how photochemistry affects the degradation of organic pollutants. This work entails the detection and quantification of reactive intermediates produced photochemically from the CDOM and their reactions with anthropogenic compounds, principally polycyclic aromatic hydrocarbons and halogenated organic compounds, in an effort to develop predictive models for the photochemical degradation of these materials. Some of that work will be continued under this grant.

REFERENCES

- Blough, N.V. and R. Del Vecchio (2002). Chromophoric dissolved organic matter in the coastal environment. In: *Biogeochemistry of Marine Dissolved Organic Matter* (D.A. Hansell and C.A. Carlson, Eds.), Academic Press, 509-546.
- Del Vecchio, R. (2002). Chromophoric dissolved organic matter (CDOM) in natural waters: Distribution, dynamics and nature. Ph.D. Thesis, University of Maryland, 240 pp.
- Del Vecchio, R. and Blough, N.V. (2002). Photobleaching of chromophoric dissolved organic matter in natural waters: Kinetics and modeling. *Mar. Chem.*, **78**, 231-253.
- Del Vecchio, R. and N.V. Blough (2002). Influence of ultraviolet radiation on the chromophoric dissolved organic matter (CDOM) in natural waters. In: *Environmental UV Radiation: Impact and Assessment, Impact on Ecosystems and Human Health* (F. Ghetti and J.F. Bornman), NATO ASI Series, in press.
- Del Vecchio, R. and N.V. Blough (in preparation). On the origin of the absorption spectrum of humic substances. To be submitted to *Environ. Sci. Technol.*
- Del Vecchio, R. and N.V. Blough (in preparation). Spatial and seasonal distribution of CDOM and DOC in the Middle Atlantic Bight. To be submitted to the special edition of *Marine Chemistry*.
- Del Vecchio, R., Subramaniam, A., Vodacek, A., Ziolkowski, L., Miller, W.L. and Blough, N.V. (in preparation). Inherent and apparent optical properties of waters in the Middle Atlantic Bight: Spatial and seasonal variability and relation to remote sensing reflectance. To be submitted to the special edition of *Marine Chemistry*.
- Vodacek, A., Blough, N.V., DeGrandpre, M.D., Peltzer, E.T., and Nelson, R.K. (1997). Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnol. Oceanogr.*, **42**, 674-686.

PUBLICATIONS

- Thomas-Smith, T.E. and N.V. Blough (2001). Photoproduction of hydrated electron from constituents of natural waters. *Environ. Sci. Technol.*, **35**, 2721-2726.
- Blough, N.V. (2001). Photochemical Processes. In: *Encyclopedia of Ocean Sciences* (J. Steele, S. Thorpe and K. Turekian, Eds.), Academic Press.
- Blough, N.V. and R. Del Vecchio (2002). Chromophoric Dissolved Organic Matter (CDOM) in the Coastal Environment. In: *Biogeochemistry of Marine Dissolved Organic Matter* (D.A. Hansell and C.A. Carlson, Eds.), Academic Press, 509-546.
- Del Vecchio, R. and N.V. Blough (2002). Photobleaching of chromophoric dissolved organic matter in natural waters: Kinetics and modeling. *Mar. Chem.*, **78**, 231-253.

Del Vecchio, R. and N.V. Blough (2002). Influence of ultraviolet radiation on the chromophoric dissolved organic matter (CDOM) in natural waters. In: *Environmental UV Radiation: Impact and Assessment, Impact on Ecosystems and Human Health* (F. Ghetti and J.F. Bornman), NATO ASI Series, in press.

Fasnacht, M.P. and N.V. Blough (2002). Aqueous photodegradation of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.*, in press (web release date, September 18th).

Moore, R.M. and N.V. Blough (2002). A marine source of methyl nitrate. *Geophys. Res. Lett.*, 10.1029/2002GL014989; web publication date, 13 Aug. 2002.

Petigara, B.R. and N.V. Blough (2002). Mechanisms of hydrogen peroxide decomposition in soils. *Environ. Sci. Technol.*, **36**, 639-645.

Pochon, A., P.P. Vaughan, D. Gan, P. Vath, N.V. Blough and D.F. Falvey (2002). Photochemical oxidation of water by 2-methyl-1,4-benzoquinone: Evidence against the formation of free hydroxyl radical. *J. Phys. Chem. A*, **106**, 2889-2894.